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Photoelectrochemical Properties of $Fe_2O_3/CuFe_2O_4$ Composite Nanorod Arrays as Photoanodes

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Solar water splitting is arguably one of the most important chemical reactions because its oxidation process produces oxygen for the world and the sun illuminates the earth with an enormous amount of energy daily. Hematite (α-Fe_2O_3) is one promising candidate for the water splitting due to its adequate absorption of visible light and stability under water oxidation conditions.[1-2] Also, hematite is nontoxic and abundant which make it a potential material for large scale applications. α-Fe_2O_3 is an n-type semiconductor that has many excellent properties for use as a photoanode in the photoelectrolyzation of water.[3] Compared to other abundant metal oxides, α-Fe_2O_3 hematite has the advantage that its bandgap is about 2.1eV allowing for the absorption of roughly 40% of the solar spectrum. Many of the desirable properties of Fe_2O_3 are shared with Fe-based ternary oxides classified as ferrites that have a chemical formula of MFe_2O_4 where M is divalent ion such as Cu^{2+} and Co^{2+}. The bandgap of ferrites is comparable to that of α-Fe_2O_3 and is also chemically and photochemically stable in basic media; consequently n-type MFe_2O_4 is promising as a photoanode for the photoelectrolysis of water. In this work, we synthesized $Fe_2O_3/CuFe_2O_4$ composite electrodes and investigated their photoelectrochemical properties as the photoanodes.

Hematite array nanorods were fabricated on FTO coated glass substrates by hydrothermal treatment of a mixture of $FeCl_3$ and $NaNO_3$ ethanol solutions with hydrochloric acid. The $Fe_2O_3/CuFe_2O_4$ composite electrodes were prepared by submerging the hematite nanorods in the solution of $Cu(NO_3)_2$ for 3 h at room temperature and then annealed in the air at 520°C for 12 h with a ramping rate of 2 °C/min. The morphologies and nanoparticle sizes of the hematite nanorods were characterized with a field emission scanning electron microscope (SEM, JEOL JSM-6700F). The hematite nanostructured films on FTO substrates were characterized with a powder X-ray diffractometer (XRD, Rigaku D/max-rA) equipped with a rotating anode and a Cu Kα radiation source (λ = 1.5406 Å). Diffraction patterns were recorded from 20 to 70° (2θ) with a step size of 0.04° at 1°/min. Hematite nanostructures were fashioned into the photoanodes by securing a copper wire onto a bare portion of FTO-coated substrates by soldering. The substrates were then sealed on all edges with epoxy resin except for a working area of 0.70 cm^2. Photoelectrochemical measurements were recorded by an electrochemical workstation (CHI 660D, CH Instruments, Inc.) using a three-electrode configuration with a hematite film as the working photoelectrode, Ag/AgCl as the reference electrode, and platinum foil as the counter electrode in 1 M NaOH. Sunlight was simulated with a 150W Xenon lamp and an AM 1.5G air mass filter (Newport, 96000 Full Spectrum Solar Simulator).

X-ray diffraction and energy-dispersive spectroscopy studies show that a crystalline $CuFe_2O_4$ phase formed after the heat treatment. As given in Fig. 1 and Fig. 2, in comparison to the bare Fe_2O_3 electrode, the $Fe_2O_3/CuFe_2O_4$ composite electrode demonstrated better photoelectrochemical performances such as enhanced photocurrent density. This can be due to the fact that $CuFe_2O_4$ has both conduction and valence band edges shifted to the negative direction, which allows for the efficient separation of electron-hole pairs at the $Fe_2O_3/CuFe_2O_4$ interface. These findings demonstrate that charge separation can be effectively promoted and photocurrent density can be dramatically increased by engineering the interface between the hematite and the electrolyte.

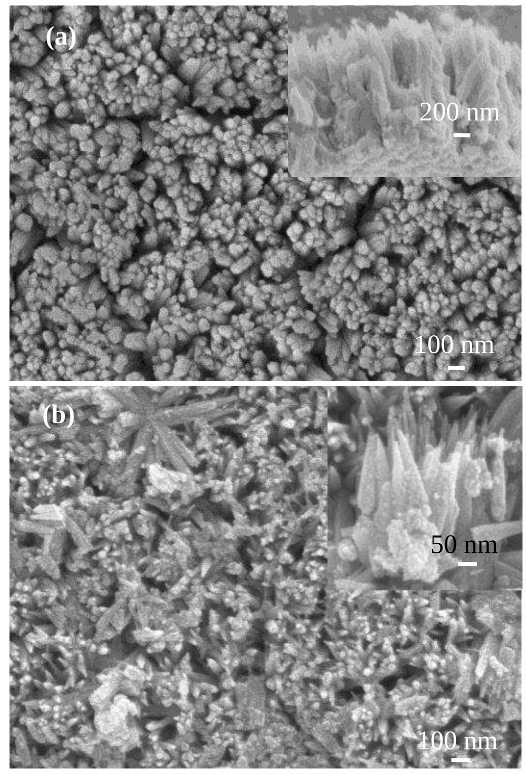

Fig.1. SEM images of array films on FTO substrates: (a) hematite and (b) α-$Fe_2O_3/CuFe_2O_4$.

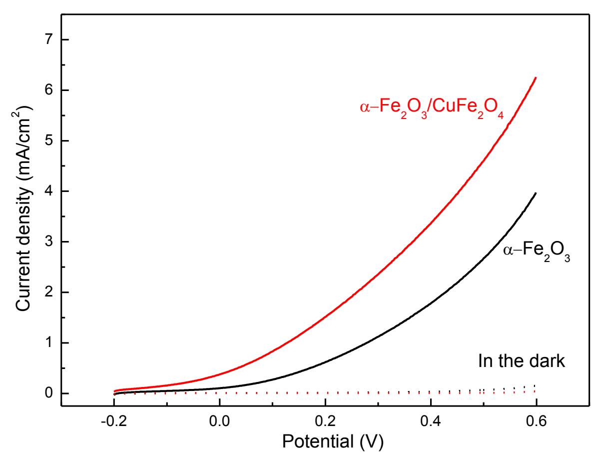

Fig.2. Photocurrent density *vs.* potential curves in the dark and under the illumination of AM 1.5G simulated solar light (100 mW/cm^2) in 1 M NaOH electrolyte (pH 13.6) with a scan rate of 10 mV/s.

Acknowledgements

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